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14. ABSTRACT

The objective of this research was the development of theoretical and computational methods to guide the design and characterization of materials relevant to the Air Force. The research centered on the development of new methodology for the simulation of hydrogen transfer reactions. The method development focused mainly on the nuclear-electronic orbital method for the incorporation of nuclear quantum effects in electronic structure calculations. Other projects included simulations of proton transfer reactions in condensed phases, calculations of vibronic couplings for self-exchange hydrogen transfer reactions, and computational studies of hydrogen bonding properties in ionic liquids. The applications of these novel computational approaches to materials relevant to the Air Force are providing information that should aid in the design and characterization of these materials. Ionic liquids are of interest to the Air Force due to the wide range of technological applications, including the development of highly energetic and environmentally benign propellants.

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Simulation of Reaction for the Design of Energetic Materials, Resistant Coatings, and Laser Protection Devices

I. Introduction

The objective of the research supported by this grant was the development of theoretical and computational methods to guide the design and characterization of materials relevant to the Air Force. The research centered on the design of new methodology for the simulation of hydrogen transfer reactions. The method development focused mainly on the nuclear-electronic orbital (NEO) method for the incorporation of nuclear quantum effects in electronic structure calculations. Other projects included simulations of proton transfer reactions in condensed phases, calculations of vibronic couplings for self-exchange hydrogen transfer reactions, and computational studies of ionic liquids, which are promising candidates for highly energetic and environmentally benign monopropellants.

II. Methods and Results

A. Nuclear-electronic orbital (NEO) method

The goal of this project was to develop the NEO method for the incorporation of nuclear quantum effects into electronic molecular orbital calculations.[1,2] In this method, specified nuclei are treated quantum mechanically on the same level as the electrons. Both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions, and the variational method is utilized to minimize the energy with respect to all molecular orbitals, as well as the centers of the nuclear basis functions. Significant correlation effects among the electrons and nuclei are included with multiconfigurational and perturbation theory methods. The NEO approach may be used to calculate structures, energies, frequencies, isotope effects, tunneling splittings, and vibronic couplings. The NEO approach is designed for the quantum mechanical treatment of a relatively small number of nuclei, such as the hydrogen nuclei involved in key hydrogen bonding interactions or hydrogen transfer reactions.

The NEO approach provides a number of advantages over the more conventional approaches. In the NEO framework, the nuclear quantum effects are incorporated during the electronic structure calculation, rather than subsequently calculated as a correction factor. Moreover, the Born-Oppenheimer separation of electrons and quantum nuclei can be avoided, and excited vibrational-electronic states may be calculated. As a result, nonadiabatic effects may be included in dynamical calculations. In addition, the NEO approach is computationally practical for a wide range of chemical reactions, and its accuracy can be improved systematically through increased basis set size and inclusion of additional correlation with larger numbers of configurations and extended methodology.

The NEO approach is particularly useful for the description of hydrogen transfer reactions. In this case, the hydrogen nuclei and all electrons are treated quantum mechanically. The minimum energy path includes nuclear quantum effects such as zero point energy and hydrogen tunneling, and the reaction coordinate reflects changes in the environment created by the classical nuclei. This approach maintains the conceptual

picture of a reaction path, while eliminating the difficulties associated with large curvature of the reaction path for the transfer of light nuclei. A number of challenges arise in the implementation of the NEO approach for hydrogen transfer reactions. Over the past grant period, we extended and enhanced the NEO method to address these challenges.

We developed new types of nuclear basis sets to calculate nuclear-electronic wavefunctions for hydrogen transfer systems.[3] We attain the greatest accuracy by representing the transferring hydrogen atom by two basis function centers to allow delocalization of the proton vibrational wavefunction. We analyzed technical issues pertaining to flexibility of the basis set to describe both single and double well proton potential energy surfaces, linear dependency of the hydrogen basis functions, multiple minima in the basis function center optimization, convergence of the number of hydrogen basis function centers, and basis set superposition error. In addition, the accuracy of the NEO approach was tested by comparison to Fourier grid calculations for the $[He-H-He]^+$ and $[He-H-He]^{++}$ model systems.

We also addressed the challenges that arise in the application of the NEO approach to hydrogen tunneling systems.[4,5] For these types of systems, typically the nuclear wavefunction is bilobal and is delocalized between the donor and the acceptor at the transition state. The calculation of delocalized, bilobal hydrogen wavefunctions and the corresponding tunneling splittings within the NEO framework is difficult due to the importance of electron-proton correlation. For a symmetric $[X–H–X]$ system, where X is a general donor and acceptor, the hydrogen moves in a symmetric double well potential for sufficiently large separations between the donor and acceptor. In the NEO approach, the hydrogen atom for this type of system is represented by two basis function centers. Based on the symmetry of this system, the exact nuclear wavefunction is expected to be delocalized equally over both basis function centers. The variational NEO-HF solution, however, corresponds to a nuclear wavefunction localized on one of the basis function centers. We demonstrated analytically that the localization of the nuclear density at the NEO-HF level is a consequence of the neglect of electron-proton correlation, which is particularly important due to the attractive electron-proton Coulomb interaction.

We showed that the inclusion of sufficient electron-proton correlation with multiconfigurational methods enables the calculation of delocalized, symmetric nuclear wavefunctions.[3-5] The NEO-full CI (NEO-FCI) approach allows the calculation of hydrogen tunneling splittings, but this approach is not computationally practical for most chemical systems due to the large number of configurations in the CI expansion. The NEO-MCSCF approach, in which the electronic and nuclear molecular orbitals as well as the CI coefficients are optimized variationally, is more computationally tractable because a smaller number of configurations is included in the CI expansion. We have shown, however, that the variational NEO-MCSCF solution is still localized for the accessible active spaces of most chemical systems.

To address this problem, we developed the state-averaged NEO multiconfigurational self-consistent-field (MCSCF) approach to obtain delocalized nuclear-electronic wavefunctions for these types of systems.[4,5] In this method, the molecular orbitals are optimized to minimize the energy of an equally weighted linear combination of the lowest two vibronic states. We applied the state-averaged NEO-MCSCF method to $[Cl–H–Cl]$, $[Cl–H–Cl]^-$, and malonaldehyde. These calculations

illustrated that this approach provides qualitatively reasonable, delocalized wavefunctions for symmetric hydrogen tunneling systems. Unfortunately, this approach is not easily applied to asymmetric systems due to difficulties in obtaining the delocalized molecular orbitals in the active space.

We also developed the NEO nonorthogonal configuration interaction (NEO-NOCI) approach for calculating delocalized hydrogen wavefunctions and the corresponding tunneling splittings.[6] The basic scheme is analogous to the nonorthogonal CI method used previously in conventional electronic structure calculations. In the two-state NEO-NOCI approach, the ground and excited state delocalized nuclear-electronic wavefunctions are expressed as linear combinations of two nonorthogonal localized nuclear-electronic wavefunctions obtained at the NEO-HF level. The tunneling splitting is determined by the energy difference between these two delocalized vibronic states. The hydrogen tunneling splittings calculated with the NEO-NOCI approach for the [He-H-He]$^+$ model system with a range of fixed He–He distances are in excellent agreement with NEO-full CI and Fourier grid calculations. The NEO-NOCI method is robust and computationally efficient, and it can be applied to asymmetric as well as symmetric systems.

In addition, we developed the NEO-MP2 (second-order perturbation theory) method for including electron-electron and electron-proton dynamical correlation.[7] We showed that removal of the proton-proton Coulomb-exchange operator from the reference Hamiltonian can lead to a significantly lower second-order energy and potentially faster convergence of the perturbation series for many-electron systems with a single quantum nucleus and many classical nuclei. Our application of the NEO-MP2 approach to the chemical systems [HeHHe]$^+$, [FHF]$^-$, and [ClHCl]$^-$ illustrated the substantial decrease in the second-order energy. Moreover, we applied the NEO-MP2 method to a set of bihalides, [XHX]$^-$, X = F, Cl, Br, and the hydrogen fluoride dimer.[8] Our analysis of these systems provided insight into the significance of electron-electron and electron-proton correlation, anharmonicity of the vibrational modes, and nonadiabatic effects for hydrogen-bonded systems.

More recently, we developed an explicitly correlated Hartree-Fock (NEO-XCHF) approach to include explicit electron-proton correlation directly into the NEO self-consistent-field framework using Gaussian-type geminal functions.[9] In contrast to previous approaches, which produce nuclear wavefunctions that are too localized and severely overestimate hydrogen vibrational frequencies, the NEO-XCHF method provides accurate nuclear wavefunctions and hydrogen vibrational stretch frequencies. The NEO-XCHF method is computationally practical for many-electron systems with a relatively small number of quantum nuclei because only electron-proton correlation is treated explicitly. Electron-electron dynamical correlation can be included with density functional theory or perturbation theory methods.

We also investigated isotope effects with the NEO approach.[10] We showed analytically that Hartree-Fock nuclear wavefunctions do not provide physically reasonable descriptions of systems comprised of equivalent low-spin fermions or equivalent bosons. The physical basis for this breakdown is that the ionic terms dominate due to the localized nature of the nuclear orbitals. Multiconfigurational wavefunctions that include only covalent terms provide physically reasonable descriptions of these types of systems. We applied the NEO approach to a variety of chemical systems to elucidate

the isotope effects on the geometries and electronic wavefunctions. Deuteration of hydrogen halides, water, ammonia, and hydronium ion decreases the bond length and the magnitude of negative partial atomic charge on the heavy atom. These results are consistent with experimental spectroscopic data. Deuteration at the beta position for formate anion and a series of amines increases the magnitude of negative partial atomic charge on the protonation site for the unprotonated species. These results are consistent with experimental observations.

The NEO approach has also been extended to model mixed positronic-electronic wavefunctions. A positron (e^+) has the same mass as but the opposite charge from an electron. Positron atomic and molecular systems have been studied previously with a variety of methods. This project is the result of a collaboration with Larry Burggraf and his graduate student, Paul Adamson, at the Air Force Institute of Technology in Dayton, Ohio. In this application, the mass of the proton was replaced with that of a positron, and Gaussian basis sets for positrons were optimized variationally for simple systems. NEO-full CI and NEO-MP2 calculations for were performed for the positronium hydride system and the e^+LiH molecule. The fundamental nature of electron-positron correlation was analyzed to pave the way for future calculations on larger systems of interest to the Air Force.

The NEO approach has been implemented in the GAMESS electronic structure program. A summary of the current capabilities of our NEO code is as follows:

1. Calculate energies and analytical gradients at the NEO-HF level.

2. Calculate energies and numerical gradients at the NEO-CI, NEO-MCSCF, state-averaged NEO-MCSCF, NEO-NOCI, and NEO-MP2 levels.

3. Calculate, project, and diagonalize the numerical Hessian.

4. Locate and characterize geometry stationary points (i.e., minima and transition states).

5. Calculate zero point energy corrections and thermodynamic properties.

6. Utilize any specified nuclear basis set with the option of multiple basis function centers.

7. Treat fermionic and bosonic nuclei, as well as positrons.

8. General options: conventional or direct calculation of integrals, RHF or ROHF treatment of electrons, symmetry, expectation values of hydrogen coordinates, population analysis.

B. Proton transfer in the condensed phase

In addition to the development of the NEO approach, we investigated issues arising in calculations of proton transfer reactions in the condensed phase. We derived an expression for the transition state theory rate constant in terms of the potential of mean force for a general reaction coordinate and the mass-weighted gradient of this reaction coordinate.[11] Similar expressions had been derived previously, but this form of the rate constant enables the straightforward calculation of rates for infrequent events with conventional umbrella sampling and free energy perturbation methods. We illustrated the

utility of this approach by an application to hydride transfer in an enzyme dihydrofolate reductase using a hybrid quantum/classical molecular dynamics method. We also applied the molecular dynamics with quantum transitions surface hopping method to a model proton transfer system in a dissipative bath and showed that the surface hopping method is in good agreement with the numerically exact results in the relatively high friction regime.[12] These results validate the use of surface hopping methods to describe proton transfer reactions in a wide range of condensed phase environments.

In addition, we investigated the ultrafast enol-keto photoisomerization in the lowest singlet excited state of 2-(2'-hydroxyphenyl)-4-methyloxazole using classical molecular dynamics in conjunction with an empirical valence bond potential.[13] We studied this process in four different environments: the gas phase, dimethyl sulfoxide, water, and human serum albumin protein. We analyzed the effects of the environment on the proton transfer time and the promoting-mode motions. The ring-ring in-plane bending of HPMO was identified as the dominant low-frequency vibrational mode that decreases the proton donor-acceptor distance to facilitate proton transfer. The mean proton transfer times were $100 - 200$ fs in all of the environments. The population decay of the enol tautomer in the S_1 state was significantly slower for the reaction in water than in DMSO and protein. The slower population decay in water was found to arise from configurations with intermolecular hydrogen bonds between HPMO and water molecules, leading to a disruption of the intramolecular hydrogen bond in HPMO. All of the condensed phase environments were found to dampen the donor-acceptor vibrational mode after the proton transfer process, thereby stabilizing the keto tautomer. In the gas phase, the donor-acceptor mode oscillations continued to facilitate the forward and reverse isomerization process.

C. Vibronic couplings for self-exchange reactions

We calculated the vibronic couplings for the phenoxyl/phenol and the benzyl/toluene self-exchange reactions with a semiclassical approach, in which all electrons and the transferring hydrogen nucleus are treated quantum mechanically.[14] In this formulation, the vibronic coupling is the Hamiltonian matrix element between the reactant and product mixed electronic-proton vibrational wavefunctions. The magnitude of the vibronic coupling and its dependence on the proton donor-acceptor distance can significantly impact the rates and kinetic isotope effects, as well as the temperature dependences, of proton-coupled electron transfer reactions.

Our calculations indicate that both of these self-exchange reactions are vibronically nonadiabatic with respect to a solvent environment at room temperature, but the proton tunneling is electronically nonadiabatic for the phenoxyl/phenol reaction and electronically adiabatic for the benzyl/toluene reaction. For the phenoxyl/phenol system, the electrons are unable to rearrange fast enough to follow the proton motion on the electronically adiabatic ground state, and the excited electronic state is involved in the reaction. For the benzyl/toluene system, the electrons can respond virtually instantaneously to the proton motion, and the proton moves on the electronically adiabatic ground state. For both systems, the vibronic coupling decreases exponentially with the proton donor-acceptor distance for the range of distances studied. When the transferring hydrogen is replaced with deuterium, the magnitude of the vibronic coupling decreases and the exponential decay with distance becomes faster. Previous studies

designated the phenoxyl/phenol reaction as proton-coupled electron transfer and the benzyl/toluene reaction as hydrogen atom transfer. In addition to providing insights into the fundamental physical differences between these two types of reactions, our analysis provides a new diagnostic for differentiating between the conventionally defined hydrogen atom transfer and proton-coupled electron transfer reactions.

D. Ionic liquids

Ionic liquids, which are typically defined to be organic salts that melt below 100 °C, have many potential technological applications because of their low vapor pressure, versatility, and environmentally benign nature. Protic ionic liquids, which are formed by proton transfer between acids and bases, are potentially relevant to high-temperature fuel cell applications. We investigated ammonium nitrate and hydroxylammonium nitrate clusters, which serve as model systems for the development of methods to study the properties of ionic liquids.[15] Ammonium nitrate has been used as a solid oxidizer in rocket propulsion fuels, and hydroxylammonium nitrate has been used in liquid propellants. Understanding the fundamental properties of these ionic materials provides the foundation for future studies of ionic liquids.

We characterized the covalent and ionic clusters of ammonium nitrate and hydroxyl ammonium nitrate using density functional theory and second-order vibrational perturbation theory.[15] The most stable structures are covalent acid-base pairs for the monomers and ionic acid-base pairs for the dimers. The hydrogen bonding distances are greater in the ionic dimers than in the covalent monomers, and the stretching frequencies are significantly different in the covalent and ionic clusters. The anharmonicity of the potential energy surfaces is found to influence the geometries, frequencies, and nuclear magnetic shielding constants for these systems. The inclusion of anharmonic effects significantly decreases many of the calculated vibrational frequencies in these clusters and improves the agreement of the calculated frequencies with the experimental data available for the isolated neutral species. The calculations of nuclear magnetic shielding constants for all nuclei in these clusters illustrate that quantitatively accurate predictions of nuclear magnetic shieldings for comparison to experimental data require the inclusion of anharmonic effects. These calculations of geometries, frequencies, and shielding constants provide insight into the significance of anharmonic effects in ionic materials and provide data that will be useful for the parameterization of molecular mechanical forcefields for ionic liquids. Anharmonic effects will be particularly important for the study of proton transfer reactions in ionic materials.

III. Summary

Thus, we have developed a variety of approaches for the simulation of hydrogen transfer reactions. The nuclear-electronic orbital (NEO) method incorporates nuclear quantum effects in electronic molecular orbital calculations and enables the calculation of structures, energies, frequencies, tunneling splittings, minimum energy paths, and direct dynamics for chemical reactions. Nonadiabatic molecular dynamics methods have been developed for the simulation of proton transfer reactions in condensed phases. Semiclassical methods have been implemented for the calculation of vibronic couplings

in proton-coupled electron transfer systems. Applications of quantum dynamical methods to ionic liquids have provided insights into the hydrogen bonding properties.

The application of these approaches to materials relevant to the Air Force is providing information that should aid in the design and characterization of these materials. These calculations elucidate the role of nuclear quantum effects such as zero point energy and hydrogen tunneling. Moreover, they provide insight into the detailed mechanisms, as well as the influence of solvent and substituents, on the rates of hydrogen transfer reactions. Such mechanistic information is critical for the efficient synthesis of these materials and the production of new functional species. Ionic liquids are of particular interest to the Air Force due to the wide range of technological applications, including the development of highly energetic and environmentally benign propellants.

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1. S. Hammes-Schiffer and N. Iordanova, "Theoretical studies of proton-coupled electron transfer reactions," *Biochim. Biophys. Acta* **1655**, 29-36 (2004).

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a. Presentations during funding period

1. Indiana University, Bloomington, Indiana, February 5, 2004 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

2. Gordon Research Conference on Isotopes in Biological and Chemical Sciences, Ventura, California, February 14-20, 2004 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

3. American Physical Society National Meeting, Montreal, Canada, March 22-26, 2004 (invited talk): "Hybrid Quantum-Classical Molecular Dynamics of Hydrogen Transfer Reactions in Enzymes"

4. American Chemical Society National Meeting, Symposium on Mixed Quantum, Classical and Semiclassical Dynamics, Anaheim, California, March 28-April 1, 2004 (invited talk): "Electron-Proton Correlation in the Nuclear-Electronic Orbital Method: Applications to Hydrogen Tunneling Systems"

5. NSF-UK N+N meeting, Washington, D.C., April 15-16, 2004 (invited talk): "Hybrid Quantum-Classical Molecular Dynamics of Enzyme Reactions"

6. University of Minnesota, Minneapolis, Minnesota, April 23, 2004 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

7. Johns Hopkins University, Baltimore, Maryland, May 4, 2004 (Ephraim and Wilma Shaw Roseman Lecturer): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

8. Canadian Society for Chemistry Conference, London, Ontario, May 29-June 1, 2004 (invited talk): "Hybrid Quantum-Classical Molecular Dynamics of Hydrogen Transfer Reactions in Enzymes"

9. Workshop on Condensed Phase Dynamics, Telluride, Colorado, July 19-23, 2004 (invited talk): "Proton-Coupled Electron Transfer"

10. MERCURY Undergraduate Research Conference, Hamilton College, July 29-31 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

11. Protein Society Annual Symposium, San Diego, California, August 15, 2004 (invited talk): "Utilization of Computational Approaches to Elucidate Enzyme Mechanisms"

12. Yale University, New Haven, Connecticut, September 14, 2004 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

13. Colorado State University, Fort Collins, Colorado, October 14, 2004 (physical chemistry seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

14. University of Colorado, Boulder, Colorado, October 15, 2004 (physical chemistry seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

15. University of Massachusetts at Amherst, Amherst, Massachusetts, November 16, 2004 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

16. Mount Holyoke College, November 17, 2004, Lucy Pickett Lecturer: "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

17. McGill University, Montreal, Canada, November 23, 2004, Donald Lecturer: "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

18. Harvard University and Massachusetts Institute of Technology, Boston, Massachusetts, December 9, 2004 (Woodward Lecture Series, Harvard/MIT physical chemistry seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

19. 19th Enzyme Mechanisms Conference, Pacific Grove, California, January 5-9, 2005 (invited talk): "Impact of Enzyme Motion on Activity"

20. Gordon Research Conference on Molecular Energy Transfer, Buellton, California, January 9-15, 2005 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

21. American Chemical Society National Meeting, Symposium on Hydrogen Bonds: Developments in Experiment and Theory, San Diego, California, March 13-17, 2005 (invited talk): "Impact of Nuclear Quantum Effects on Hydrogen Bonding and Proton Transfer Reactions"

22. Princeton University, Princeton, New Jersey, March 31, 2005 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

23. Duke University, Durham, North Carolina, April 5, 2005 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

24. University of Toronto, Chemical Biophysics Symposium, April 8-10, 2005 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

25. University of Michigan, Ann Arbor, Michigan, April 21, 2005 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

26. Texas A&M University, College Station, Texas, May 5, 2005 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

27. Mathematical Biosciences Institute, Workshop on Enzyme Dynamics, Ohio State University, May 19-21, 2005 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

28. AFOSR contractor's meeting, Monterey, California, May 22-25, 2005 (invited talk): "Impact of Nuclear Quantum Effects on Hydrogen Bonding and Proton Transfer Reactions"

29. American Conference on Theoretical Chemistry, Los Angeles, California, July 16-21, 2005 (invited talk): "Proton-Coupled Electron Transfer: Analysis of Dynamics and Calculations of Couplings"

30. American Chemical Society National Meeting, Symposium on Electron Transfer Processes: Making Connections, Washington, D.C., August 28-September 1, 2005 (invited talk): "Proton-Coupled Electron Transfer Reactions in Solution and Proteins"

31. American Chemical Society National Meeting, Symposium on Theoretical Determination of Energy Landscapes: Methodology and Applications, Washington, D.C., August 28-September 1, 2005 (invited talk): "Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations"

32. University of Houston, Houston, Texas, September 14, 2005 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

33. University of Texas at Austin, Austin, Texas, September 15, 2005 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

34. Baker Symposium, Cornell University, Ithaca New York, October 1, 2005 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

35. University of Maryland, College Park, Maryland, October 5, 2005 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

36. Royal Society Discussion Meeting on Quantum Catalysis in Enzymes – Beyond the Transition State Theory Paradigm, London, November 14-15, 2005 (invited talk) "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

37. November 16, 2005: Chair the Novartis Foundation Royal Society Discussion Meeting on "Computational Approaches to H-Transfer"

38. Pacifichem Conference, Symposium on Nonadiabatic Phenomena and Related Dynamics: Theory and Experiment, Honolulu, Hawaii, December 15-20, 2005 (invited talk): "Nonadiabatic Proton-Coupled Electron Transfer Reactions in Solution and Proteins"

39. Pacifichem Conference, Symposium on Proton Transfer/Transport: H-bonded Solids, Liquids, Clusters, and Interfaces, Honolulu, Hawaii, December 15-20, 2005 (invited talk): "Hybrid Quantum-Classical Molecular Dynamics of Hydrogen Transfer Reactions in Enzymes"

40. Gordon Research Conference on Metals in Biology, Ventura, California, January 29-February 2, 2006 (invited talk): "Proton-Coupled Electron Transfer Reactions in Solution and Proteins"

41. Biophysical Society Annual Meeting, Salt Lake City, Utah, February 18-22, 2006 (invited talk): "Impact of Enzyme Motion on Activity"

42. American Chemical Society National Meeting, Symposium on Quantum Molecular Dynamics in the Condensed Phase: Towards Bridging the Gap between Theory and Experiment, Atlanta, Georgia, March 26-30, 2006 (invited talk): "Proton-Coupled Electron Transfer and Hydrogen Atom Transfer in the Condensed Phase"

43. Argonne National Laboratory, Argonne, Illinois, April 10, 2006 (seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

44. University of Texas Southwestern Medical Center, Dallas, Texas, April 13, 2006 (seminar): "Impact of Enzyme Motion on Activity"

45. DARPA Protein Design Processes Program Review, Islamorada, Florida, April 18-20, 2006 (invited talk): "Ranking Protein Designs According to Chemical Reaction Barriers"

46. New York University, New York, New York, April 28, 2006 (colloquium): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

47. Oak Ridge National Laboratory, Oak Ridge, Tennessee, May 10, 2006 (seminar): "Proton-Coupled Electron Transfer Reactions in Solution and Proteins"

48. 12th International Congress of Quantum Chemistry (ICQC), Kyoto, Japan, May 21-26, 2006 (invited talk): "Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations"

49. ICQC satellite meeting on Reactions in Solution and Biological Systems: Potential Energy Surface and Dynamics, Kyoto, Japan, May 27-29, 2006 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

50. Gordon Research Conference on Vibrational Spectroscopy: Probing Structure and Dynamics, Biddeford, Maine, July 2-7, 2006 (invited talk): "Proton-Coupled Electron Transfer Reactions in Solution and Proteins"

51. Gordon Research Conference on Atomic and Molecular Interactions, New London, New Hampshire, July 9-14, 2006 (invited talk): "Nuclear-Electronic Orbital Approach: Calculation of Structures, Frequencies, and Couplings"

52. Telluride Workshop on Condensed Phase Dynamics, Telluride, Colorado, July 17-23, 2006 (invited talk): "Nuclear-Electronic Orbital Approach: Calculation of Structures, Frequencies, and Couplings"

53. American Chemical Society National Meeting, Symposium entitled Beyond Michael Dewar's Legacy: Modern Semiempirical MO Theory, San Francisco, California, September 10-14, 2006 (invited talk): "Impact of Enzyme Motion on Activity"

54. American Chemical Society National Meeting, Symposium entitled Fifty Years of Electron Transfer and RRKM Theories, San Francisco, California, September 10-14, 2006 (invited talk): "Proton-Coupled Electron Transfer: Couplings, Rates, and Isotope Effects"

55. Michigan State University, East Lansing, Michigan, October 6, 2006 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

56. California Institute of Technology, Pasadena, California, November 28, 2006 (invited seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

b. Consultative and advisory functions

None

c. Transitions

None

New discoveries, inventions, or patent disclosures

None

Honors/Awards

International Academy of Quantum Molecular Science Medal, 2005

Iota Sigma Pi Agnes Fay Morgan Research Award, 2005

Alexander M. Cruickshank Lecturer, Gordon Research Conference on Isotopes in Biological & Chemical Sciences, 2004

Ephraim and Wilma Shaw Roseman Lecturer, Johns Hopkins University, 2004

Lucy Pickett Lecturer, Mount Holyoke College, 2004

Donald Lecturer, McGill University, 2004

Woodward Lecturer, Harvard University, 2004

Senior Editor for *The Journal of Physical Chemistry*, 2001 - present

Editorial Advisory Board for *Accounts of Chemical Research*, 2006 - present

Advisory Board for *Theoretical Chemistry Accounts*, 2002 - present

Vice-Chair/Chair, Theoretical Subdivision of the American Chemical Society, 2002 - 2005